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NMR relaxation study of the phase transitions and relaxation mechanisms of the alums $M\mathrm{Cr}(\mathrm{SO_4})_2\cdot 12\mathrm{H_2O}$ (M=Rb and Cs) single crystals

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ABSTRACT

The physical properties and phase transition mechanisms of $M\mathrm{Cr(SO_4)_2\cdot 12H_2O}$ (M=Rb and Cs) single crystals have been investigated. The phase transition temperatures, NMR spectra, and the spin-lattice relaxation times T_1 of the ^{87}Rb and ^{133}Cs nuclei in the two crystals were determined using DSC and FT NMR spectroscopy. The resonance lines and relaxation times of the ^{87}Rb and ^{133}Cs nuclei undergo significant changes at the phase transition temperatures. The sudden changes in the splitting of the Rb and Cs resonance lines are attributed to changes in the local symmetry of their sites, and the changes in the temperature dependences of T_1 are related to variations in the symmetry of the octahedra of water molecules surrounding $\mathrm{Rb^+}$ and $\mathrm{Cs^+}$. We also compared these ^{87}Rb and ^{133}Cs NMR results with those obtained for the trivalent cations Cr and Al in $M\mathrm{Cr(SO_4)_2\cdot 12H_2O}$ and $M\mathrm{Al(SO_4)_2\cdot 12H_2O}$ crystals.

1. Introduction

The alums can be represented with the general formula $M^+Me^{3+}(\mathrm{SO_4})_2\cdot 12\mathrm{H_2O}$, where M is a monovalent cation such as Na, K, Rb, Cs, or $\mathrm{NH_4}$, and Me is a trivalent cation such as Al, Fe, or Cr [1,2]. The alums investigated in this study were $M^+Me^{3+}(\mathrm{SO_4})_2\cdot 12\mathrm{H_2O}$ (M=Rb, Cs and Me=Cr, Al). Alums are classified as α, β, or γ, which correspond to three slightly different arrangements of the ions and molecules within the cubic lattice [3]. Common to the three subtypes is the arrangement of the M^+ and Me^{3+} ions, which form a cubic face-centered lattice. M^+ and Me^{3+} ions are each surrounded by six $\mathrm{H_2O}$ molecules. The Me^{3+} ions are surrounded by almost regular octahedra of $\mathrm{H_2O}$. The orientation of this octahedron with respect to the crystal axes is slightly different for α-, β-, and γ-alums [4]. If the M cation is small, a γ-alum forms. The only known representative of this class is $\mathrm{NaCr(SO_4)_2\cdot 12H_2O}$. A β-alum forms if the M cation is large, such as in $\mathrm{CsCr(SO_4)_2\cdot 12H_2O}$, and an α-alum, which is by far the most common type, forms if the M cation is medium, such as in $\mathrm{KCr(SO_4)_2\cdot 12H_2O}$, $\mathrm{RbCr(SO_4)_2\cdot 12H_2O}$, and $\mathrm{NH_4Cr(SO_4)_2\cdot 12H_2O}$ [5,6]. The $M^+(\mathrm{H_2O})_6$ octahedra in γ-alums are quite regular. In the α-alums, the $M^+(\mathrm{H_2O})_6$ octahedra are distorted by a flattening parallel to one of the threefold axes, and in the β-alums the distortion leads to an almost planar arrangement of the six $\mathrm{H_2O}$ molecules around the central ion M^+.

The phase transition temperatures of $\mathrm{RbCr(SO_4)_2\cdot 12H_2O}$ and $\mathrm{CsCr(SO_4)_2\cdot 12H_2O}$ crystals have not previously been established. A variety of salts with interesting properties have been studied with many methods in recent years. Some questions, however, have not yet been resolved, especially those related to the nature of their phase transitions. The connection between the crystal structures and the thermal stabilities of the alums has been discussed by Cudey [7]. The quadrupole coupling constants of ^{87}Rb and ^{133}Cs in $M\mathrm{Cr(SO_4)_2\cdot 12H_2O}$ and $M\mathrm{Al(SO_4)_2\cdot 12H_2O}$ (M=Rb and Cs) crystals have been reported using the static nuclear magnetic resonance (NMR) method by Weiden and Weiss [8,9]; in the cases of $\mathrm{RbCr(SO_4)_2\cdot 12H_2O}$ and $\mathrm{RbAl(SO_4)_2\cdot 12H_2O}$, the quadrupole coupling constants of the ^{87}Rb nucleus were found to be 12.735 and 13.221 MHz, respectively, and the quadrupole coupling constant of the ^{133}Cs nucleus in $\mathrm{CsAl(SO_4)_2\cdot 12H_2O}$ was found to be 229.5 kHz. Although the electron paramagnetic resonance (EPR) and NMR studies of $M\mathrm{Al(SO_4)_2\cdot 12H_2O}$ (M=Rb and Cs) at room temperature have been carried out [10–18], the physical properties and phase transition temperatures of $M\mathrm{Cr(SO_4)_2\cdot 12H_2O}$ (M=Rb and Cs) single crystals have not yet been reported.

In the present study, the NMR spectra and spin-lattice relaxation times, T_1, for ^{87}Rb and ^{133}Cs nuclei in $\mathrm{RbCr(SO_4)_2\cdot 12H_2O}$ and $\mathrm{CsCr(SO_4)_2\cdot 12H_2O}$ single crystals were obtained. In addition, we investigated the phase transitions of these crystals using

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differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), optical polarizing microscopy, and NMR. To probe the phase transitions that occur in the two single crystals, the measurement of the ^{87}Rb and ^{133}Cs relaxation times was preferred, because the ^{87}Rb and ^{133}Cs relaxation times are likely to be very sensitive to changes in the symmetry of these crystals. This is the first time that the phase transitions of $RbCr(SO_4)_2 \cdot 12H_2O$ and $CsCr(SO_4)_2 \cdot 12H_2O$ crystals have been investigated, and we use these results to analyze the environments of the Rb and Cs nuclei. We also compare our results for $MCr(SO_4)_2 \cdot 12H_2O$ (M=Rb and Cs) with those for $MAl(SO_4)_2 \cdot 12H_2O$ crystals, which have a similar structure. The comparison of the effects of Cr and Al on their respective alum crystals is an interesting area of study. Therefore, this work significantly enhances understanding of the relaxation processes and the nature of phase transitions occurring in these crystals.

2. Crystal structure

The structures of $MCr(SO_4)_2 \cdot 12H_2O$ (M=Rb and Cs) crystals have previously been determined using X-ray diffraction [19–21]. These single crystals have cubic structures and belong to the space group $Pa\bar{3}$, with four molecules per unit cell. The lattice parameters of $RbCr(SO_4)_2 \cdot 12H_2O$ and $CsCr(SO_4)_2 \cdot 12H_2O$ crystals are $a=b=c=12.296$ and 12.352 Å, respectively. The M^+ and Cr^{3+} ions in $MCr(SO_4)_2 \cdot 12H_2O$ crystals are each surrounded by six water molecules, as shown in Fig. 1 [19]. The nearest neighbors of Cr^{3+} are six water molecules, which form a nearly regular octahedron. In contrast, the octahedron of water molecules about M^+ is strongly distorted.

3. Experimental method

The $MCr(SO_4)_2 \cdot 12H_2O$ (M=Rb and Cs) single crystals were prepared by the slow evaporation of aqueous solutions at 293 K. The $MCr(SO_4)_2 \cdot 12H_2O$ specimens are hexagonal with dimensions of $4 \times 4 \times 3$ mm^3.

The structures of $RbCr(SO_4)_2 \cdot 12H_2O$ and $CsCr(SO_4)_2 \cdot 12H_2O$ single crystals at room temperature were determined with an X-ray diffractometer system (Bruker AXS GMBH) at the Korea Basic Science Institute. And, in order to determine the phase transition temperatures, DSC was carried out on the crystals using a Dupont 2010 DSC instrument. Measurements were made at a heating rate of 10 °C/min. TGA was carried out on the crystals using a Sinco TGA-1000 instrument. In addition, the NMR measurements for the ^{87}Rb and ^{133}Cs nuclei in the $MCr(SO_4)_2 \cdot 12H_2O$ single crystals were obtained with the 400 FT NMR spectroscopy at the Korea Basic Science Institute. The static magnetic field was 9.4 T, and the central radio frequency was set at $\omega_0/2\pi=130.90$ MHz for the ^{87}Rb nucleus and at $\omega_0/2\pi=52.48$ MHz for the ^{133}Cs nucleus. The spin-lattice relaxation times were measured using a saturation recovery pulse sequence, sat–t–$\pi/2$: the nuclear magnetizations of the ^{87}Rb and ^{133}Cs nuclei at time t after the sat pulse, a comb of one hundred of $\pi/2$ pulses applied at a regular interval of 10 μs, were determined following the excitation $\pi/2$ pulse. The widths of the $\pi/2$ pulses were 1 s for ^{87}Rb and 1.65 μs for ^{133}Cs. The temperature-dependent NMR measurements were carried out over the temperature range 180–420 K. The samples were maintained at constant temperatures by controlling the nitrogen gas flow and the heater current. The temperature controller was calibrated using the temperature dependence of the chemical shift of ^{207}Pb nucleus in $Pb(NO_3)_2$ at a temperature range 150–500 K [22]. The precision of the sample temperature was within ±1 K at the experimental range 180–420 K.

4. Experimental results and analysis

4.1. ^{87}Rb NMR for $RbCr(SO_4)_2 \cdot 12H_2O$ single crystals

From our X-ray diffraction result, the structure of a $RbCr(SO_4)_2 \cdot 12H_2O$ crystal was found to have cubic symmetry with cell parameters $a=b=c=12.278$ Å. This result is consistent with that of Figgis et al. [19]. Optical polarizing microscopy was used to show that the color of these crystals varies with temperature: dark purple at room temperature, light purple near 400 K, and dark green near 460 K. This variation in color might be related to the loss of H_2O. Two endothermic peaks were found with DSC for $RbCr(SO_4)_2 \cdot 12H_2O$ at 374 and 425 K, as shown in Fig. 2. TGA was used to determine whether the high-temperature transformations are structural phase transitions or chemical reactions. The thermogram of $RbCr(SO_4)_2 \cdot 12H_2O$ is shown in the inset in Fig. 2. The mass loss begins in the vicinity of 330 K, and transformation at 330 K ($=T_d$) is due to the onset of partial thermal decomposition. Also, we checked for premelting with optical polarizing microscopy. We conclude that the endothermic peaks at 374 K (T_{C1}) and 425 K (T_{C2}) correspond to phase transitions.

The NMR spectrum of ^{87}Rb ($I=3/2$) in $RbCr(SO_4)_2 \cdot 12H_2O$ was obtained at a frequency of $\omega_0/2\pi=130.90$ MHz. When such crystals are rotated about the crystallographic axis, the crystallographically equivalent nuclei would be expected to give rise to three lines: one central line and two satellite lines. Instead of one central resonance line, four central resonance lines were obtained for the $RbCr(SO_4)_2 \cdot 12H_2O$ crystal. The signals were obtained with the magnetic field applied along the crystallographic c-axis.

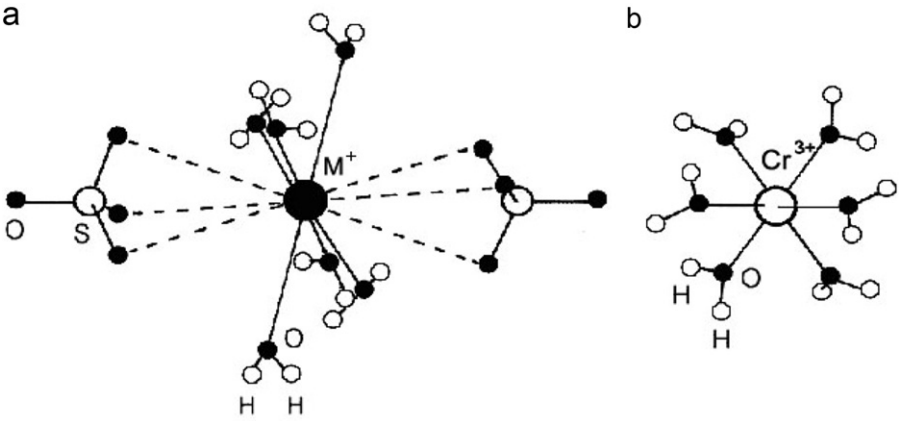

Fig. 1. Environments of (a) M^+ and (b) Cr^{3+} in $MCr(SO_4)_2 \cdot 12H_2O$ (M=Rb and Cs) at room temperature.